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PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference P/5129.WO JAT	FOR FURTHER ACTION <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. PCT/GB 99/ 02413	International filing date (day/month/year) 26/07/1999	(Earliest) Priority Date (day/month/year) 27/07/1998
Applicant IMPERIAL COLLEGE OF SCIENCE, TECHNOLOGY...et al		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.
☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

THERMAL BARRIER COATING WITH THERMOLUMINESCENT INDICATOR MATERIAL EMBEDDED THEREIN

5. With regard to the **abstract**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1
☐ None of the figures.

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Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

The abstract has to be changed as follows:

Line 1, after "component (10)" insert ", especially a gas turbine or a part thereof,":

Line 4, after "component." add:

"In a preferred embodiment, the coating consists of yttrium aluminium garnet (YAG) or yttrium stabilised zirconium. The dopant is preferably a rare earth metal, e.g. Eu, Tb, Dy."

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INTERNATIONAL SEARCH REPORT

International Application No

PC 99/02413

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C30/00 G01K11/20 G01K11/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C G01K C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 730 528 A (ALLISON STEPHEN W ET AL) 24 March 1998 (1998-03-24)	1,3-5, 7-10,14, 15,18-21
Y	abstract	6,11,13
A	column 1, line 18 - line 21 column 1, line 42 - line 49 column 2, line 1 - line 39 column 3, line 30 - line 49 column 4, line 19 - line 49 column 5, line 7 - column 6, line 41 column 7, line 62 - column 8, line 13 column 8, line 47 - line 56 claims; figures --- -/--	16,17



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

27 September 1999

Date of mailing of the international search report

06/10/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Ceulemans, J

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/99/02413

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 569 570 A (BROGARDH TORGNY ET AL) 11 February 1986 (1986-02-11)	6,11,13
A	abstract column 1, line 7 - line 14 column 1, line 43 - column 2, line 21 column 3, line 16 - line 24 column 4, line 4 - line 15 claims 1-4; figures 1,3,4,7 ---	18,19,21
A	US 4 075 493 A (WICKERSHEIM KENNETH A) 21 February 1978 (1978-02-21) the whole document ---	1,4,5, 7-10,18, 19,21
A	WO 98 10459 A (ADVANCED VISION TECHNOLOGIES I ; POTTER MICHAEL D (US)) 12 March 1998 (1998-03-12) abstract; claims 7,8,10-12,20,21; figure 7 example 4, p.15-19 ---	1,2,7-13
P,A	EP 0 863 396 A (HOWMET RESEARCH CORP) 9 September 1998 (1998-09-09) cited in the application the whole document -----	1-4,6-8, 12-21

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INTERNATIONAL SEARCH REPORT

Information on patent family members

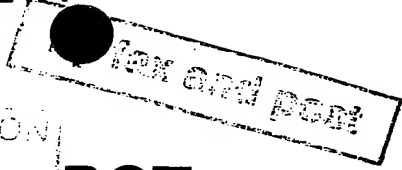
International Application No

PCT/JP 99/02413

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5730528	A	24-03-1998	US 5885484 A	23-03-1999
US 4569570	A	11-02-1986	SE 431128 B	16-01-1984
			CA 1205300 A	03-06-1986
			EP 0095673 A	07-12-1983
			JP 58215509 A	15-12-1983
			SE 8203297 A	16-01-1984
US 4075493	A	21-02-1978	CA 1098335 A	31-03-1981
			CA 1108428 A	08-09-1981
			DE 2755713 A	22-06-1978
			FR 2374624 A	13-07-1978
			FR 2482292 A	13-11-1981
			GB 1605117 A	16-12-1981
			GB 1605118 A	16-12-1981
			GB 1605116 A	16-12-1981
			JP 1535451 C	21-12-1989
			JP 53101480 A	04-09-1978
			JP 63063845 B	08-12-1988
WO 9810459	A	12-03-1998	AU 4330897 A	26-03-1998
			CA 2239288 A	12-03-1998
EP 0863396	A	09-09-1998	NONE	

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PATENT COOPERATION TREATY



From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

SOUTHAMPTON
DEC 08 2000

PCT

To:

BODEN, Keith
D. Young & Co.
21 New Fetter Lane
London EC4A 1DA
GRANDE BRETAGNE

MONTH	11
DAY	05
YEAR	2000
DD - 7 JUL 2001	
APPRO	
ENTRY	
FOR	KMB

**NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**
(PCT Rule 71.1)

Date of mailing (day/month/year)	05.12.2000
-------------------------------------	------------

Applicant's or agent's file reference
P005129WO KMB

IMPORTANT NOTIFICATION

International application No. PCT/GB99/02413	International filing date (day/month/year) 26/07/1999	Priority date (day/month/year) 27/07/1998
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Applicant
IMPERIAL COLLEGE OF SCIENCE, TECHNOLOGY...et al

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

<p>Name and mailing address of the IPEA/ European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465</p>	<p>Authorized officer Krage, D Tel. +49 89 2399-7530</p>
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Corrected
Version

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P005129WO KMB	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB99/02413	International filing date (day/month/year) 26/07/1999	Priority date (day/month/year) 27/07/1998
International Patent Classification (IPC) or national classification and IPC C23C30/00		
Applicant IMPERIAL COLLEGE OF SCIENCE, TECHNOLOGY...et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 5 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 02/02/2000	Date of completion of this report 05.12.2000
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Hahn, H Telephone No. +49 89 2399 8450 

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB99/02413

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

Description, pages:

1-10 as originally filed

Claims, No.:

1-19 as received on 10/10/2000 with letter of 05/10/2000

Drawings, sheets:

1/7-7/7 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☒ the claims, Nos.: 20-21

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB99/02413

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 1-19
	No: Claims
Inventive step (IS)	Yes: Claims 1-19
	No: Claims
Industrial applicability (IA)	Yes: Claims 1-19
	No: Claims

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/02413

1. Section V:

The applicant's second submission of arguments as well as the new set of claims 1-19 as submitted with the letter dated 05.10.00 - that is more than one month after the set time limit given in the second written opinion - crossed with the first IPER completed on 23.11.00.

However, since this set of claims 1-19 was more clearly distinguished particularly with respect to documents D1 and D2 these arguments and claims were eventually considered and this second corrected IPER was written based on these claims 1-19.

1.1 The claims 1-15 and 17-19 of this application are interpreted as product claims 'per se'. Therefore any document which discloses such a claimed product (i.e. a machine component having somewhere a coating of a mixture of a refractory material and an indicator material or a thermal barrier coating material comprising a mixture of a refractory material and an indicator material) - even if used for a different purpose - takes away the novelty of the claimed subject-matter.

1.2 Document D1 discloses a high temperature phosphor of the general formula $\text{LuPO}_4:\text{Dy}_{(x)},\text{Eu}_{(y)}$ which is coated onto turbine engine components and used in combination with excitation caused by a laser to determine the temperature of the said component (cf. abstract; figure 1; col. 1, lines 11-15 and lines 52-56; col. 3, lines 30-67; col. 4, lines 29-40; col. 5, line 7 to col. 6, line 41). D1 does not disclose a combination of the said phosphor $\text{LuPO}_4:\text{Dy}_{(x)},\text{Eu}_{(y)}$ with a refractory material.

Contrarily to the applicant's allegations D1 discloses other thermally sensitive phosphor materials that belong to the state of the art which comprise yttrium oxide doped with Eu and yttrium aluminium garnet doped with either Dy, Sm, Tb or Eu (i.e. YAG:Dy, YAG:Sm, YAG:Tb, YAG:Eu) (cf. col. 8, lines 47-52) which have been used at high temperatures above 600°C. YAG represents a refractory material. However, D1 does neither disclose a thermal barrier coating material comprising such a mixture nor the use of such mixture as a thermal barrier coating.

1.2.3 The applicant argued in his letter that "there is, however, absolutely no disclosure or suggestion of the use of those thermally sensitive phosphor materials as a **thermal**

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/02413

barrier coating material for a machine component". These arguments are now fully accepted because amended claim 1 defines "a thermal barrier coating". The same conclusion is valid for the use claim 16 and the product claims 17-19 referring back to said use claim.

1.3 Document D2 discloses an optical sensor for detecting changes in physical quantities such as temperature, position, force, level, pressure, flow, acceleration, magnetic or electrical field strength or mechanical deformation including a luminescent material such as Nd ions or some rare earth metal forming a solid solution in glass or some crystalline material, e.g. yttrium-aluminium-garnet (YAG) (cf. abstract; col. 1, lines 7-14 and line 43 to col. 2, line 21; col. 3, lines 16-24; col. 4, lines 4-15; col. 5, line 33 to col. 6, line 5; claims 1-7).

The implicitly disclosed solid solution of atomically localized luminescence centres in a monocrystalline bonding material, e.g. rare earth doped YAG, according to D2 does, however, not suggest any thermal barrier coating comprising the said solid solution.

1.4 Thus the subject-matter of the claims is not readily derivable for the skilled person when combining the teaching of documents D1 and D2.

1.5 As a consequence of the paragraphs 1.1 to 1.4 above the claims 1-19 are considered to meet the requirements of Article 33(2) and (3) PCT. The industrial applicability of the subject-matter claimed is self-evident.

2. Section VII:

The description has not been adapted to the new claims in order to provide a clear support for them. Furthermore, the documents D1 and D2 are not additionally identified in the description and briefly discussed therein so that the requirements of Rule 5.1(a)(ii) PCT are not met.

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CLAIMS

1. A machine component coated with a thermal barrier coating, wherein the thermal barrier coating comprises a mixture of at least a refractory material and an indicator material having an optical emission spectrum which varies in response to the temperature of at least a region of the component.
5
2. A component according to claim 1, wherein the component is coated with one or more priming layers over which the thermal barrier coating is coated.
- 10 3. A component according to claim 1 or 2, wherein the indicator material has an optical emission spectrum which varies in response to a physical parameter of the component.
- 15 4. A component according to claim 3, wherein the indicator material has an optical emission spectrum which varies in response to at least one physical parameter selected from the group consisting of a physical strain applied to at least a region of the component, erosion of at least a region of the component, and a physical stress of at least a region of the component.
- 20 5. A component according to any of claims 1 to 4, wherein the refractory material is selected from the group consisting of yttria stabilised zirconia, yttria partially stabilised zirconia, and yttria aluminium garnet.
- 25 6. A component according to any of claims 1 to 5, wherein the indicator material is a phosphor material.
7. A component according to any of claims 1 to 5, wherein the indicator material comprises a rare earth dopant.

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8. A component according to claim 7, wherein the indicator material comprises a dopant selected from the group consisting of terbium, europium, and dysprosium.
- 5 9. A component according to any of claims 1 to 8, wherein the indicator material comprises a compositionally-graded structure, a composite structure, or a multi-phase structure.
- 10 10. A component according to any of claims 1 to 9, wherein the thermal barrier coating comprises a layered structure of indicator materials having different respective emission spectra.
- 15 11. A component according to any of claims 1 to 10, wherein the thermal barrier coating comprises a layered structure of an outermost, substantially transparent region and a region including an indicator material optically interrogatable through the substantially transparent region.
- 20 12. A component according to any of claims 1 to 11, wherein the component is a component of a combustion engine.
13. A component according to claim 12, wherein the component is a component of a gas turbine engine.
- 25 14. A component according to claim 13, wherein the component is a turbine blade.
15. A component according to claim 13, wherein the component is a heat shield.
- 30 16. Use, as a thermal barrier coating for coating a machine component, of a mixture of at least a refractory material and an indicator material having an optical emission spectrum which varies in response to a physical parameter of the coated component.

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17. A machine having one or more internal components coated with a thermal barrier coating according to claim 16, the machine comprising:
a light source for directing an interrogating light beam onto the one or more
5 components; and
a light collector for collecting light from the one or more components.
18. A machine according to claim 17, further comprising an analyser for detecting a
physical property of the one or more components by analysis of light collected
10 from the one or more components.
19. A machine according to claim 17 or 18, wherein the machine is a combustion engine.

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PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C.20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year)

25 February 2000 (25.02.00)

International application No.

PCT/GB99/02413

Applicant's or agent's file reference

P/5129.WO JAT

International filing date (day/month/year)

26 July 1999 (26.07.99)

Priority date (day/month/year)

27 July 1998 (27.07.98)

Applicant

CHOY, Kwang-Leong et al

1. The designated Office is hereby notified of its election made:

☒

in the demand filed with the International Preliminary Examining Authority on:

02 February 2000 (02.02.00)

☐

in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Olivia RANAIVOJAONA

Telephone No.: (41-22) 338.83.38

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 07 DEC 2000

WIPO

PCT

Applicant's or agent's file reference P005129WO KMB	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB99/02413	International filing date (day/month/year) 26/07/1999	Priority date (day/month/year) 27/07/1998
International Patent Classification (IPC) or national classification and IPC C23C30/00		
Applicant IMPERIAL COLLEGE OF SCIENCE, TECHNOLOGY...et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.



☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☐ Certain observations on the international application

**CORRECTED
VERSION**

Date of submission of the demand 02/02/2000	Date of completion of this report 05.12.2000
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Hahn, H Telephone No. +49 89 2399 8450 

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/02413

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

Description, pages:

1-10 as originally filed

Claims, No.:

1-19 as received on 10/10/2000 with letter of 05/10/2000

Drawings, sheets:

1/7-7/7 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☒ the claims, Nos.: 20-21

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/02413

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-19
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-19
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-19
	No:	Claims	

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

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1. Section V:

The applicant's second submission of arguments as well as the new set of claims 1-19 as submitted with the letter dated 05.10.00 - that is more than one month after the set time limit given in the second written opinion - crossed with the first IPER completed on 23.11.00.

However, since this set of claims 1-19 was more clearly distinguished particularly with respect to documents D1 and D2 these arguments and claims were eventually considered and this second corrected IPER was written based on these claims 1-19.

1.1 The claims 1-15 and 17-19 of this application are interpreted as product claims 'per se'. Therefore any document which discloses such a claimed product (i.e. a machine component having somewhere a coating of a mixture of a refractory material and an indicator material or a thermal barrier coating material comprising a mixture of a refractory material and an indicator material) - even if used for a different purpose - takes away the novelty of the claimed subject-matter.

1.2 Document D1 discloses a high temperature phosphor of the general formula $\text{LuPO}_4:\text{Dy}_{(x)}\text{Eu}_{(y)}$ which is coated onto turbine engine components and used in combination with excitation caused by a laser to determine the temperature of the said component (cf. abstract; figure 1; col. 1, lines 11-15 and lines 52-56; col. 3, lines 30-67; col. 4, lines 29-40; col. 5, line 7 to col. 6, line 41). D1 does not disclose a combination of the said phosphor $\text{LuPO}_4:\text{Dy}_{(x)}\text{Eu}_{(y)}$ with a refractory material.

Contrarily to the applicant's allegations D1 discloses other thermally sensitive phosphor materials that belong to the state of the art which comprise yttrium oxide doped with Eu and yttrium aluminium garnet doped with either Dy, Sm, Tb or Eu (i.e. YAG:Dy, YAG:Sm, YAG:Tb, YAG:Eu) (cf. col. 8, lines 47-52) which have been used at high temperatures above 600°C. YAG represents a refractory material. However, D1 does neither disclose a thermal barrier coating material comprising such a mixture nor the use of such mixture as a thermal barrier coating.

1.2.3 The applicant argued in his letter that "there is, however, absolutely no disclosure or suggestion of the use of those thermally sensitive phosphor materials as a thermal

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barrier coating material for a machine component". These arguments are now fully accepted because amended claim 1 defines "a thermal barrier coating". The same conclusion is valid for the use claim 16 and the product claims 17-19 referring back to said use claim.

1.3 Document D2 discloses an optical sensor for detecting changes in physical quantities such as temperature, position, force, level, pressure, flow, acceleration, magnetic or electrical field strength or mechanical deformation including a luminescent material such as Nd ions or some rare earth metal forming a solid solution in glass or some crystalline material, e.g. yttrium-aluminium-garnet (YAG) (cf. abstract; col. 1, lines 7-14 and line 43 to col. 2, line 21; col. 3, lines 16-24; col. 4, lines 4-15; col. 5, line 33 to col. 6, line 5; claims 1-7).

The implicitly disclosed solid solution of atomically localized luminescence centres in a monocrystalline bonding material, e.g. rare earth doped YAG, according to D2 does, however, not suggest any thermal barrier coating comprising the said solid solution.

1.4 Thus the subject-matter of the claims is not readily derivable for the skilled person when combining the teaching of documents D1 and D2.

1.5 As a consequence of the paragraphs 1.1 to 1.4 above the claims 1-19 are considered to meet the requirements of Article 33(2) and (3) PCT. The industrial applicability of the subject-matter claimed is self-evident.

2. Section VII:

The description has not been adapted to the new claims in order to provide a clear support for them. Furthermore, the documents D1 and D2 are not additionally identified in the description and briefly discussed therein so that the requirements of Rule 5.1(a)(ii) PCT are not met.

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CLAIMS

1. A machine component coated with a coating material, the coating material comprising a mixture of at least a refractory material and an indicator material having a optical emission spectrum which varies in response to the temperature of the coated component.
5
2. A component according to claim 1, the component being coated with one or more priming layers, the coating material being applied over the one or more priming layers.
10
3. A component according to claim 1 or claim 2, in which the coating material is an outermost, thermally insulating coating material.
4. A component according to any one of the preceding claims, the indicator material having a optical fluorescence emission spectrum which varies in response to a physical parameter of the coated component.
15
5. A component according to any one of the preceding claims, in which the indicator material has an emission spectrum which varies in dependence on the temperature of at least a region of the coated component.
20
6. A component according to any one of the preceding claims, in which the indicator material has an emission spectrum which varies in dependence on at least one parameter selected from the group consisting of:
25
 - (i) a physical strain applied to at least a region of the coated component;
 - (ii) erosion of at least a region of the coated component;
 - (iii) a physical stress of at least a region of the coated component;
 - (iv) a physical strain applied to at least a region of the coated component.

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7. A component according to any one of the preceding claims, in which the refractory material is selected from the group consisting of yttria stabilised zirconia, yttria partially stabilised zirconia and yttria aluminium garnet.

5 8. A component according to any one of the preceding claims, in which the indicator material is a phosphor material.

9. A component according to any one of the preceding claims, in which the indicator material comprises a rare earth dopant.

10

10. A component according to claim 9, in which the indicator material comprises a dopant selected from the group consisting of terbium, europium and dysprosium.

15

11. A component according to any one of the preceding claims, in which the coating material comprises a layered structure of indicator materials having different respective emission spectra.

20

12. A component according to any one of the preceding claims, in which the coating material comprises a layered structure of an outermost substantially transparent region and a region of indicator material arranged to be optically interrogatable through the substantially transparent region.

25

13. A component according to any one of the preceding claims, in which the indicator material comprises a compositionally graded structure, a composite structure or a multi-phase structure.

14. A component according to any one of the preceding claims, the component being a component of a combustion engine.

30

15. A component according to claim 14, the component being a component of a gas turbine engine.

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16. A component according to claim 15, in which the component is a turbine blade.

17. A component according to claim 15, in which the component is a heat shield.

5

18. A thermal barrier coating material for coating a machine component, the coating material comprising a mixture of at least a refractory material and an indicator material having an optical emission spectrum which varies in response to a physical parameter of the coated component.

10

19. A machine having one or more internal components coated with a coating according to claim 18, the machine comprising:

a light source for directing an interrogating light beam onto the coated component(s); and

15

a light collector for collecting light from the coated component(s).

20. A machine according to claim 19, the machine being a combustion engine.

21. A machine according to claim 19 or claim 20, comprising an analyser for
20 detecting a physical property of the coated component(s) by analysis of light collected from the component(s).

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RECD 27 NOV 2000

W.P.C. P.C.T.

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P005129WO KMB	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB99/02413	International filing date (day/month/year) 26/07/1999	Priority date (day/month/year) 27/07/1998
International Patent Classification (IPC) or national classification and IPC C23C30/00		
Applicant IMPERIAL COLLEGE OF SCIENCE, TECHNOLOGY...et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 6 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 02/02/2000	Date of completion of this report 23.11.2000
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Hahn, H Telephone No. +49 89 2399 8450 

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/02413

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

Description, pages:

1-10 as originally filed

Claims, No.:

1-20 as received on 10/08/2000 with letter of 06/08/2000

Drawings, sheets:

1/7-7/7 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☒ the claims, Nos.: 21

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/02413

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-16,18-20
	No:	Claims	17
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-20
Industrial applicability (IA)	Yes:	Claims	1-20
	No:	Claims	

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/02413

1. Section V:

The applicant's arguments as submitted with the fax dated 06.08.00 - that is more than one month after the set time limit - with respect to document D1 have been carefully considered based on the rewritten claims 1-20. Effectively, the scope of said claims has not been changed by the cosmetic amendments. The applicant's letter of reply was totally silent with respect to the novelty and lack of inventive step objections based on document D2.

1.1 The claims 1-20 of this application are interpreted as product claims 'per se'. Therefore any document which discloses such a claimed product (i.e. a machine component having somewhere a coating of a mixture of a refractory material and an indicator material or a thermal barrier coating material comprising a mixture of a refractory material and an indicator material) - even if used for a different purpose - takes away the novelty of the claimed subject-matter.

1.2 Document D1 discloses a high temperature phosphor of the general formula $\text{LuPO}_4:\text{Dy}_{(x)},\text{Eu}_{(y)}$ which is coated onto turbine engine components and used in combination with excitation caused by a laser to determine the temperature of the said component (cf. abstract; figure 1; col. 1, lines 11-15 and lines 52-56; col. 3, lines 30-67; col. 4, lines 29-40; col. 5, line 7 to col. 6, line 41). D1 does not disclose a combination of the said phosphor $\text{LuPO}_4:\text{Dy}_{(x)},\text{Eu}_{(y)}$ with a refractory material.

However, contrarily to the applicant's allegations D1 discloses other thermally sensitive phosphor materials that belong to the state of the art which comprise yttrium oxide doped with Eu and yttrium aluminium garnet doped with either Dy, Sm, Tb or Eu (i.e. YAG:Dy, YAG:Sm, YAG:Tb, YAG:Eu) (cf. col. 8, lines 47-52) which have been used at high temperatures above 600°C. YAG represents a refractory material.

1.2.1 These specified mixtures of the prior art thus meet all the requirements of the wording of composition claim 'per se' 17. Claim 17 thus lacks novelty with respect to D1. The applicant's attention in this context is directed to the claims 6 and 9 of the present application which specify the use of YAG as the refractory material and the use of Dy, Tb or Eu as the indicator material.

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1.2.2 Furthermore, the use of these materials in combination with a laser source for determining the fluorescence emission for the same purpose (i.e. e.g. turbine engine components) as the specific phosphor material $\text{LuPO}_4:\text{Dy}_{(x)},\text{Eu}_{(y)}$ claimed by D1 appears to be obvious for the skilled person. Thus the subject-matter of the claims 18-20 - defining such a component with a fluorescence measuring device for determining the temperature of the said component - lacks an inventive step. Absolutely the same conclusion is fully valid for the subject-matter of the claims 1, 3-4, 6-9 and 13-16 - only being directed to the machine components coated with such an indicator material - which thus lack an inventive step, too.

1.2.3 The applicant argued in his letter that "there is, however, absolutely no disclosure or suggestion of the use of those thermally sensitive phosphor materials as **a thermal barrier coating material** for a machine component". This might be true but claim 1 does nowhere define "a thermal barrier coating". Furthermore, claim 1 does not define the extent of the said coating. The requirement of the present wording of claim 1 is already fulfilled if there is somewhere a coated area comprising the said - known - mixture according to D1 or D2 for the purpose of temperature measurement. Consequently, the applicant's arguments have no counterpart in the claims and thus cannot be accepted.

1.3 Document D2 discloses an optical sensor for detecting changes in physical quantities such as temperature, position, force, level, pressure, flow, acceleration, magnetic or electrical field strength or mechanical deformation including a luminescent material such as Nd ions or some rare earth metal forming a solid solution in glass or some crystalline material, e.g. yttrium-aluminium-garnet (YAG) (cf. abstract; col. 1, lines 7-14 and line 43 to col. 2, line 21; col. 3, lines 16-24; col. 4, lines 4-15; col. 5, line 33 to col. 6, line 5; claims 1-7).

1.3.1 The implicitly disclosed solid solution of atomically localized luminescence centres in a monocrystalline bonding material, e.g. rare earth doped YAG, according to D2 is novelty destroying for claim 17.

1.3.2 The embodiment according to figure 3 of D2 has 2 layers of said indicator material which implies that - in order to represent two separate layers - must have a different composition. Thus the subject-matter of the claims 5, 10 and 11 is readily

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/02413

derivable for the skilled person when combining the teaching of documents D1 and D2. Therefore the subject-matter of the claims 5, 10 and 11 is considered to lack an inventive step with respect to such a combination of D2 and D1. It is also not apparent that the subject-matter of the claims 2 and 12 - when combined with claim 1 - set forth subject-matter which involves an inventive step with respect to the conventional and ordinary design capabilities of the skilled person in this specific technical area.

1.4 As a consequence of the paragraphs 1.1 to 1.3 above claim 17 does not meet the requirements of Article 33(2) and (3) PCT while the claims 1-16 and 18-20 do not meet the requirement of Article 33(3) PCT. The industrial applicability of the subject-matter claimed is self-evident.

2. Section VII:

The description has not been adapted to the new claims in order to provide a clear support for them. Furthermore, the documents D1 and D2 are not additionally identified in the description and briefly discussed therein so that the requirements of Rule 5.1(a)(ii) PCT are not met.

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CLAIMS

1. A machine component coated with a coating of a coating material, wherein the coating material comprises a mixture of at least a refractory material and an indicator material having an optical emission spectrum which varies in response to the temperature of at least a region of the component.
5
2. A component according to claim 1, wherein the component is coated with one or more priming layers over which the coating of the coating material is coated.
- 10 3. A component according to claim 1 or 2, wherein the coating of the coating material is an outermost, thermal barrier coating.
4. A component according to any of claims 1 to 3, wherein the indicator material has an optical emission spectrum which varies in response to a physical parameter of the component.
15
5. A component according to claim 4, wherein the indicator material has an optical emission spectrum which varies in response to at least one physical parameter selected from the group consisting of a physical strain applied to at least a region of the component, erosion of at least a region of the component, and a physical stress of at least a region of the component.
20
6. A component according to any of claims 1 to 5, wherein the refractory material is selected from the group consisting of yttria stabilised zirconia, yttria partially stabilised zirconia, and yttria aluminium garnet.
25
7. A component according to any of claims 1 to 6, wherein the indicator material is a phosphor material.

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8. A component according to any of claims 1 to 6, wherein the indicator material comprises a rare earth dopant.
- 5 9. A component according to claim 8, wherein the indicator material comprises a dopant selected from the group consisting of terbium, europium, and dysprosium.
- 10 10. A component according to any of claims 1 to 9, wherein the indicator material comprises a compositionally-graded structure, a composite structure, or a multi-phase structure.
- 15 11. A component according to any of claims 1 to 10, wherein the coating of the coating material comprises a layered structure of indicator materials having different respective emission spectra.
- 20 12. A component according to any of claims 1 to 11, wherein the coating of the coating material comprises a layered structure of an outermost, substantially transparent region and a region including an indicator material optically interrogatable through the substantially transparent region.
- 25 13. A component according to any of claims 1 to 12, wherein the component is a component of a combustion engine.
14. A component according to claim 13, wherein the component is a component of a gas turbine engine.
15. A component according to claim 14, wherein the component is a turbine blade.
16. A component according to claim 14, wherein the component is a heat shield.

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17. A thermal barrier coating material for coating a machine component, wherein the coating material comprises a mixture of at least a refractory material and an indicator material having an optical emission spectrum which varies in response to a physical parameter of the coated component.
- 5
18. A machine having one or more internal components coated with a coating of a coating material according to claim 17, the machine comprising:
a light source for directing an interrogating light beam onto the one or more components; and
10 a light collector for collecting light from the one or more components.
19. A machine according to claim 18, further comprising an analyser for detecting a physical property of the one or more components by analysis of light collected from the one or more components.
- 15
20. A machine according to claim 18 or 19, wherein the machine is a combustion engine.

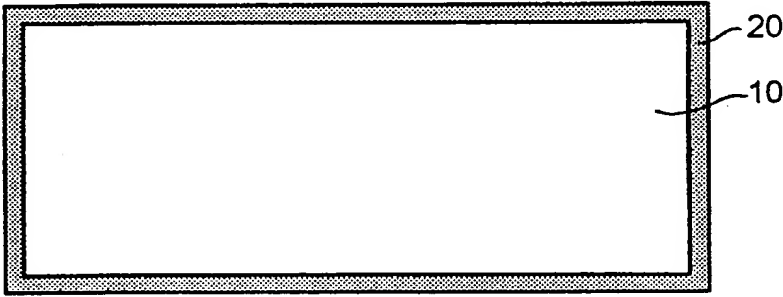
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(71) Applicant (for all designated States except US): IMPERIAL COLLEGE OF SCIENCE, TECHNOLOGY AND MEDICINE [GB/GB]; Sherfield Building, Exhibition Road, London SW7 2AZ (GB).			Published With international search report.
(72) Inventors; and			
(75) Inventors/Applicants (for US only): CHOY, Kwang-Leong [MY/GB]; 35 Blondvil Street, Cheylesmore, Coventry CV3 5EQ (GB). HEYES, Andrew, Lawrence [GB/GB]; 13 Spencers Lane, Cookham, Berkshire SL6 9JX (GB). FEIST, Joerg [DE/GB]; 67 Morley Road, Stratford, London E15 3HF (GB).			
(74) Agent: TURNER, James, Arthur; D. Young & Co., 21 New Fetter Lane, London EC4A 1DA (GB).			
(54) Title: THERMAL BARRIER COATING WITH THERMOLUMINESCENT INDICATOR MATERIAL EMBEDDED THEREIN			
(57) Abstract			
<p>A coating material (20) for coating a machine component (10), especially a gas turbine or a part thereof, comprises a mixture of at least a refractory material and an indicator material having an optical emission (e.g. fluorescence) spectrum which varies in response to a physical parameter of the coated component. In a preferred embodiment, the coating consists of yttrium aluminium garnet (YAG) or yttrium stabilised zirconium. The dopant is preferably a rare earth metal, e.g. Eu, Tb, Dy.</p>			
			

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THERMAL BARRIER COATING WITH THERMOLUMINESCENT INDICATOR MATERIAL EMBEDDED THEREIN

This invention relates to coatings, such as thermal barrier coatings.

In extreme environments such as the interior of a gas turbine engine, where the flame temperature can be greater than the melting point of materials used to construct the engine, metal components are often coated with a material to avoid or reduce thermal damage to the components. Such a coating is commonly known as a thermal barrier coating or TBC.

A thermal barrier coating typically comprises a relatively "thick" layer of a refractory or thermally insulating material such as yttria stabilised zirconia or YSZ. Here, the term "thick" is used to imply a thickness of, say, 250µm. The refractory material would generally be selected to have a low thermal conductivity such as around 1 to 3 W/mK, thereby reducing heat transfer to the components and reducing the temperature experienced by the components.

The coatings are applied using a deposition technique. Generally speaking, the deposition techniques in commercial use are not completely reliable and do not provide the level of adhesion of the coating to the component which would be desirable. This means that the lifetime of coated components is limited, but as there is no reliable model for predicting that lifetime, nor a convenient way to monitor the coatings in service, the only way to assess the state of coated components is manual inspection. In the case of a gas turbine engine, this is clearly time consuming and expensive.

A typical regime for coating a machine component with a thermal barrier coating is to apply a sandwich of three types of coating. First, a so-called bondcoat is applied. A typical material for the bondcoat is a metallic layer such as an MCrAlY alloy layer. The purpose of the bondcoat is to provide a layer which adheres well to the underlying component surface and which provides a good base for further coatings. Onto the bondcoat a so-called intermediate layer or interlayer is applied. A ceramic material such as Al₂O₃ is one example of a suitable material. This can be formed by oxidising the surface of the bondcoat to form a thin (e.g. 0.1 to 10 µm) oxide layer. Again, this provides improved adhesion for the final thermally insulating coating and is not there to provide thermal barrier properties.

The bondcoat and the interlayer may be referred to generally as priming layers, as their main purpose is to improve adhesion and application of the final, thermally insulating layer.

The final layer provides the thermal insulating and structural properties of the TBC. As mentioned above, this may be a relatively thick layer of a material such as YSZ, YPSZ (Yttria partially stabilised zirconia, e.g. 6-8 wt% Y_2O_3 PSZ) or zirconia doped alumina. Basically the outer layer should ideally be: thermally insulating (and so could be referred to as a refractory material), have low thermal conductivity, be resistant to spalling during thermal cycling and/or exposure to high temperatures (e.g. over 1100 °C), be resistant to oxidation and be resistant to erosion.

So, for example, the material of the interlayer (e.g. Al_2O_3) is not suitable for use as the outermost layer because its reliability is not good enough and because it lacks the "transformation toughening" obtainable with YPSZ.

EP-A-0 863 396 discloses a technique for detecting stress in an interlayer of the type of structure described above. It is noted that Cr impurities, originating in the bondcoat, are often present in the interlayer. EP-A-0 863 396 makes use of the change in the fluorescence wavelength of these impurities in response to stress. A light source is directed through the thermally insulating layer onto the interlayer and the resulting fluorescence wavelength is detected.

US-A-4 922 113, US-A-5 270 116 and EP-A-0 336 029 disclose techniques for monitoring the composition, thickness or uniformity of a coating by detecting fluorescence radiation.

This invention provides a machine component coated with a coating material, the coating material comprising a mixture of at least a thermally insulating material and an indicator material having an optical emission spectrum which varies in response to a physical parameter of the coated component.

The invention addresses the above difficulties by providing a new type of coating, suitable for use as a thermal barrier coating. The coating itself comprises not only a refractory material but also an indicator material having an optical emission (e.g. fluorescence) spectrum dependent on a physical parameter of the coated component such as temperature. This allows in-situ interrogation and remote

monitoring of the physical parameter by directing a light beam onto the component and analysing the fluorescence spectrum using known analysing equipment.

Unlike the arrangement of EP-A-0 863 396, the indicator material can form part of the actual TBC layer rather than an interlayer. This means that the temperature, stress etc. of the TBC layer can be monitored rather than that of the interlayer alone. This can enable the detection of faults across the top (TBC) coating and at the interface between the TBC coating and the interlayer or other priming coating.

The variation in spectrum can be, for example, a variation of absolute intensity, relative intensity between two or more emission lines, decay time of one or more emission lines after excitation by a pulsed light source, or even lineshifting due to expansion and contraction of the host crystal lattice.

The invention has many advantages over another previously proposed technique involving painting special phosphor-loaded paints onto components. Because the indicator material forms part of the coating, it can be much more resistant to erosion and thermal shock than a surface layer of paint. A separate painting process is not required. Also, the indication given by the indicator material better reflects the true condition of the coated component, rather than just a surface condition of the phosphor paint.

Although coating materials could be selected to respond to other physical parameters of the coated component, such as pressure, preferred embodiments of the invention finds particular use in allowing remote monitoring of the temperature of the component, by employing an indicator material having a fluorescence spectrum which varies in dependence on the temperature of at least a region of the coated component. In particular it is noted that the documents listed above are not concerned with temperature measurement. However, embodiments of the invention encompass materials which respond to two or more physical parameters, perhaps in different ways.

Preferably, rather than a homogeneous layer of indicator material, the indicator material comprises a layered structure of indicator materials having different respective fluorescence spectra. This arrangement has many advantages. Firstly, as the coating erodes from the component, a further layer of indicator material will be newly uncovered. As this has a distinguishable spectrum, the erosion process can therefore

be detected. In another application, the arrangement could allow monitoring of the component's temperature at different depths within the coating, particularly if lower layers of indicator material were covered by materials which are at least partially transparent to the light involved.

5 The invention finds a particular preferred use in high temperature components in, for example, a combustion engine, preferably in coating one or more turbine blades or heat shields of a gas turbine engine. In combustion engines, ambient conditions are extreme and the effort involved in manually inspecting internal components means that the inspection process can be expensive.

10 The invention also provides a coating material for coating a machine component, the coating material comprising a mixture of at least a refractory material and an indicator material having an optical emission spectrum which varies in response to a physical parameter of the coated component.

15 The invention also provides a combustion engine having one or more internal components coated with the above, the engine having a measurement system comprising a light source for directing an interrogating light beam onto the coated component(s); and a light collector for collecting light from the coated component(s).

Embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

20 Figure 1 is a schematic diagram of a coated component;

 Figure 2 is a schematic diagram of a gas turbine engine incorporating a coated component and having a remote sensing apparatus;

 Figure 3 illustrates a fluorescence spectrum for YAG:Tb;

25 Figures 4 and 5 illustrate the variation of decay lifetime with temperature for an emission of YAG:Tb;

 Figure 6 illustrates a fluorescence spectrum for Y₂O₃:Eu;

 Figures 7 and 8 illustrate the variation of decay lifetime with temperature for an emission of Y₂O₃:Eu;

30 Figures 9 and 10 illustrate the relative variation of emission linestrengths with temperature for YAG:Dy;

Figure 11 is a schematic diagram of a multi-layer indicator material providing erosion information; and

Figure 12 is a schematic diagram of a multi-layer indicator material providing temperature monitoring at different coating depths.

5 Figure 1 is a schematic diagram of a component 10 coated with a thermal barrier coating (TBC) 20. The component 10 may be, for example, a turbine blade of a gas turbine engine, although the technique is applicable to many other types of component.

10 The TBC 20 is formed as a mixture of a refractory material and an indicator material which has a fluorescence spectrum which varies in dependence on a physical parameter of the component such as temperature.

15 The coated component is particularly suited for remote monitoring of the physical parameter by directing an interrogating light beam on to the component and then analysing the fluorescence emissions returned from the component. Figure 2 is a schematic diagram of a gas turbine engine incorporating the coated component and employing a remote sensing apparatus to detect the fluorescence spectrum of the component.

20 In Figure 2, the coated component 10 is mounted on a turbine assembly 30 inside a casing 40 of the gas turbine engine. An interrogating light beam is generated by an Nd:YAG pulsed laser 50 and directed along an optical fibre waveguide 60 to a window 70 in the casing 40 of the turbine engine, from where it is directed onto the path of the component under test.

25 When the light strikes the component as it rotates past the window 70, the component's coating emits a fluorescence spectrum which is picked up by a further optical fibre 80 through a further window 90 in the casing 40. The light is passed to a detector 100.

30 An arrangement of lenses (not shown) can be used to collimate or otherwise vary the optical properties of the interrogating beam and/or the fluorescence emission. The optical fibre 60 and the optical fibre 80 can direct light through the same window in the casing 40 if desired, and, through use of a directional optical fibre coupler, the

interrogating beam and the collected fluorescence spectrum can pass along the same fibre.

The laser 50 and the detector 100 are under the control of a pulse generator and control circuit 110. The detector 100 converts the received optical signal into an electrical signal 120 which is passed to an analyser 130 arranged to detect spectral characteristics to be described below using known analysis techniques. The output of the analyser 130 is passed to an output device 140 such as a display screen or a print-out device.

The TBC is applied using a known technique such as chemical vapour deposition (CVD), electron beam physical vapour deposition (EBPVD), plasma spray deposition or electrostatic assisted vapour deposition (see, for example, WO97/21848). In this last technique, a precursor solution is directed onto the substrate (the component) and forms a deposited layer under heat treatment. An initial bondcoat and an interlayer (as described above but not shown in the drawings) may be deposited first to improve the adhesion and/or structural properties of the TBC coating.

The layer used in these embodiments is formed primarily of a refractory material but containing dopants, such as rare earth dopants, to provide the required fluorescence properties. Therefore, a straightforward way of applying such a coating is to add the rare earth dopants to the precursor solution before the electrostatic assisted vapour deposition coating process takes place. In further embodiments to be described below (see Figures 11 and 12) the composition of the indicator component varies across the depth of the coating. This type of graded or multi-phase structure can be achieved easily by varying the composition of the precursor solution during the coating process - perhaps by changing the concentration of a particular dopant by adding the dopant or adding more undoped precursor solution, or by changing from one receptacle of solution having a first dopant to another receptacle of solution having a second dopant (or no dopant), and so on. In the examples discussed below, the proportion of the dopant in the deposited layer is relatively small, so that the physical properties of the deposited layer and the deposition process itself are relatively unchanged by the addition of the dopant.

In other words, the addition of the rare earth to the thermally insulating layer in effect creates a new phosphor. This is very different to a technique for adding a phosphor to a layer material.

In a YSZ or YPSZ system the rare earths can also act to further stabilise the zirconia, improving the mechanical properties of the coating.

Two main techniques for assessing temperature by interrogating the coated components' fluorescence spectrum will be discussed below. These are a life time decay method and an intensity ratio method.

For the purposes of this example, three compositions will be discussed. $\text{Y}_2\text{O}_3:\text{Eu}$ and $\text{YAG}:\text{Tb}$ are described for the "lifetime decay method". These materials show good luminescence, are readily available and relatively cheap. Their useable temperature range goes from below 550°C to above 1200°C .

The "intensity ratio method" will be described with relation to $\text{YAG}:\text{Dy}$ material. This material has the possibility of performing two dimensional temperature distribution analysis up to temperatures of about 1500°C . Because the main emission lines of interest are below 500nm , at high temperatures black body radiation from material is still not as intense as for similar measurements with $\text{Y}_2\text{O}_3:\text{Eu}$ and $\text{YAG}:\text{Tb}$.

Lifetime Decay Method

Figure 3 is a graph of the emission spectrum for $\text{YAG}:\text{Tb}$ at different temperatures in response to an excitation wavelength of 266nm . It will be seen that the spectrum varies in magnitude with temperature. However, the feature that will be analysed in the present example is the decay time of an emission after excitation.

When the material is excited by a pulse from the pulsed laser 50, it starts to fluoresce and emit the spectrum shown in Figure 3. When the excitation pulse is removed, the intensity dies away exponentially. A characteristic time (τ) of the decay process is the time in which the intensity falls to $1/e$ of its original intensity. So, τ becomes numerically smaller as the decay becomes faster.

Figure 4 is a graph of the decay time τ versus temperature for $\text{YAG}:\text{Tb}$ at an emission wavelength of 543.1nm , an excitation wavelength of 266nm , and a Tb concentration of 5%, over a range from substantially room temperature through to

about 1000°C. It can be seen that the characteristic time tau varies in dependence on the temperature of the material.

Figure 5 is an expanded graph of the region from about 700°C to about 1000°C. This is a region of interest for the temperature analysis of components in a combustion engine, and the graph shows that there is a generally monotonic between tau and temperature. Accordingly, the detector 100 can be arranged to detect intensity of the optical signal returned from the component 10 (Figure 2) and the analyser 130 can be arranged to detect the characteristic decay time, i.e. the time in which the intensity decays by a factor of 1/e. This can then be compared - for example via a look-up table - with the results of Figure 5 to determine the temperature of the component 10.

Figure 7 illustrates the exponential decay process for an emission from $Y_2O_3:Eu$ with temperature. The concentration of Eu is 6%, although a range of 1-6% is useful, the excitation wavelength 266nm and the emission is measured is at 611nm.

When the results of Figure 7 are converted into a graph of the characteristic decay time tau versus temperature, it can be seen that in a temperature range of interest (above 700°C) there is a useful variation of tau with temperature. This information can be used as described above in the analyser 130 of Figure 2.

Intensity Ratio Method

Figure 9 illustrates the scaled fluorescence spectrum for YAG:Dy at different temperatures. (The spectrum includes two "rogue" data points, marked as "dead pixels"). The Dy concentration is 3%.

In a steady state emission (not a fluorescence emission), the ratio of intensities for two emission wavelengths (493nm and 455nm) in response to excitation at 355nm is plotted against ambient temperature of the coated component in Figure 10. This shows a useful, almost linear relationship between the ratio and the temperature.

In Figure 10, sets of results obtained on different days are shown. These are day "j9th", the day of fabrication, and the next three days j10th to j12th. The results show a good stability of response with time.

The examples described above have related to single-layer coatings. However, as mentioned earlier, the composition of the indicator material can be varied during deposition of the TBC so as to give a TBC having multi-layer properties as regards the

indicator material but single-layer properties as regards the thermal barrier protection. Figures 11 and 12 schematically illustrate two examples of such a multi-layer indicator structure.

Referring to Figure 11, the component 10 is coated with a TBC 200 having three indicator layers within it, 210, 220, 230. The three indicator layers are formed using different indicator dopants.

This technique is very useful to assess erosion of the TBC. In Figure 11, erosion has taken place at a site 240, so that areas of the interior indicator layers 220, 210 are exposed. When the eroded component is interrogated using the light beam as described above, emission spectra will be observed corresponding to all three of the indicator 210, 220, 230. This can be used to indicate that erosion has taken place as far as the layer 210. When this occurs, a warning signal can be issued to the equipment operator (e.g. a maintenance engineer maintaining a gas turbine engine) that it is time to dismantle the engine to replace the eroded component.

Figure 12 illustrates a similar multi-layer structure having a three-indicator layer TBC formed of indicator layers 250, 260, 270. The three layers again have different respective fluorescence properties when interrogated by the interrogating light beam. A region 280 of the outer layer 270 is arranged to be substantially transparent (or at least partially transparent to the interrogating wavelength and the emission spectrum. This allows the temperature at a position inside the TIC (the position of the indicator layer 260 to be monitored. Similarly, a region 290 of the outer two layers 270, 260 is made at least partially transparent, so that the temperature of the interior layer 250 can be assessed, giving a closer indication of the temperature of the component 10 itself.

Such a multi-layer structure will also enable the heat flux to the component to be calculated assuming that the thermal conductivity of the intervening layer is known:

$$q'' = (-k \Delta T) / L$$

where k is thermal conductivity, ΔT is the temperature change and L is the thickness of the layer.

In other embodiments a compositionally graded structure can be used (by varying the indicator material composition and/or concentration during deposition), or alternatively a composite or multi-phase structure can be employed.

Embodiments of the invention can provide a TBC with indicating properties
5 which can be used to assess or measure the erosion, temperature distribution, heat flux, phase changes, pressure, stress and/or strain characteristics of a coated component, besides performing as a TBC.

The concentration of the indicator material is preferably relatively low so that its presence has little effect on the thermal properties of the TBC, but preferably high
10 enough that the spectra can be conveniently observed. A preferred range is about 0.1%-10%, although concentrations outside of that range can be envisaged.

A further dopant regime forming an embodiment of the invention is Y_2O_3 - Er (or other rare earth/s), YSZ with one or more rare earths or YPSZ with one or more rare earths.

15 Although embodiments of the invention have been described for use in non-invasive *in-situ* measurements, the techniques are also applicable to quality control and testing during coating development. If the detected temperature profile indicates a large variation across the top coat, this will create a large temperature mismatch and generate stresses in the coating material potentially leading to failure of the coating.

20 The large variation could be due to non-uniformities in the coating or an exposure to a non-uniform thermal environment. In quality control, if the coating has not been deposited uniformly, this can cause a non-uniform temperature, stress and/or strain distribution in the coating and so cause failure. Again, this can be detected using the techniques described above.

CLAIMS

1. A machine component coated with a coating material, the coating material comprising a mixture of at least a refractory material and an indicator material having a optical emission spectrum which varies in response to the temperature of the coated component.
2. A component according to claim 1, the component being coated with one or more priming layers, the coating material being applied over the one or more priming layers.
3. A component according to claim 1 or claim 2, in which the coating material is an outermost, thermally insulating coating material.
4. A component according to any one of the preceding claims, the indicator material having a optical fluorescence emission spectrum which varies in response to a physical parameter of the coated component.
5. A component according to any one of the preceding claims, in which the indicator material has an emission spectrum which varies in dependence on the temperature of at least a region of the coated component.
6. A component according to any one of the preceding claims, in which the indicator material has an emission spectrum which varies in dependence on at least one parameter selected from the group consisting of:
- (i) a physical strain applied to at least a region of the coated component;
 - (ii) erosion of at least a region of the coated component;
 - (iii) a physical stress of at least a region of the coated component;
 - (iv) a physical strain applied to at least a region of the coated component.

7. A component according to any one of the preceding claims, in which the refractory material is selected from the group consisting of yttria stabilised zirconia, yttria partially stabilised zirconia and yttria aluminium garnet.
- 5 8. A component according to any one of the preceding claims, in which the indicator material is a phosphor material.
9. A component according to any one of the preceding claims, in which the indicator material comprises a rare earth dopant.
- 10 10. A component according to claim 9, in which the indicator material comprises a dopant selected from the group consisting of terbium, europium and dysprosium.
11. A component according to any one of the preceding claims, in which the
15 coating material comprises a layered structure of indicator materials having different respective emission spectra.
12. A component according to any one of the preceding claims, in which the
coating material comprises a layered structure of an outermost substantially transparent
20 region and a region of indicator material arranged to be optically interrogatable through the substantially transparent region.
13. A component according to any one of the preceding claims, in which the
indicator material comprises a compositionally graded structure, a composite structure
25 or a multi-phase structure.
14. A component according to any one of the preceding claims, the component being a component of a combustion engine.
- 30 15. A component according to claim 14, the component being a component of a gas turbine engine.

16. A component according to claim 15, in which the component is a turbine blade.
17. A component according to claim 15, in which the component is a heat shield.
- 5 18. A thermal barrier coating material for coating a machine component, the coating material comprising a mixture of at least a refractory material and an indicator material having an optical emission spectrum which varies in response to a physical parameter of the coated component.
- 10 19. A machine having one or more internal components coated with a coating according to claim 18, the machine comprising:
- a light source for directing an interrogating light beam onto the coated component(s); and
- 15 a light collector for collecting light from the coated component(s).
20. A machine according to claim 19, the machine being a combustion engine.
- 20 21. A machine according to claim 19 or claim 20, comprising an analyser for detecting a physical property of the coated component(s) by analysis of light collected from the component(s).

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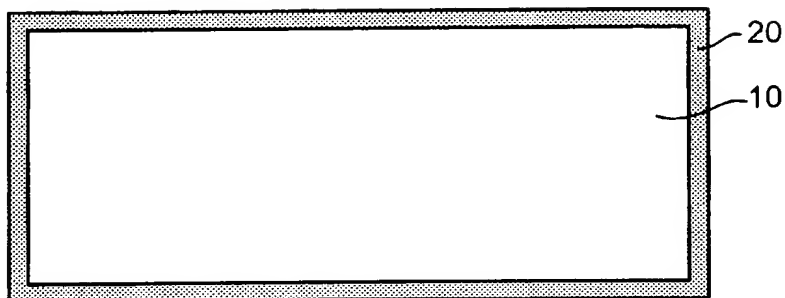


FIG. 1

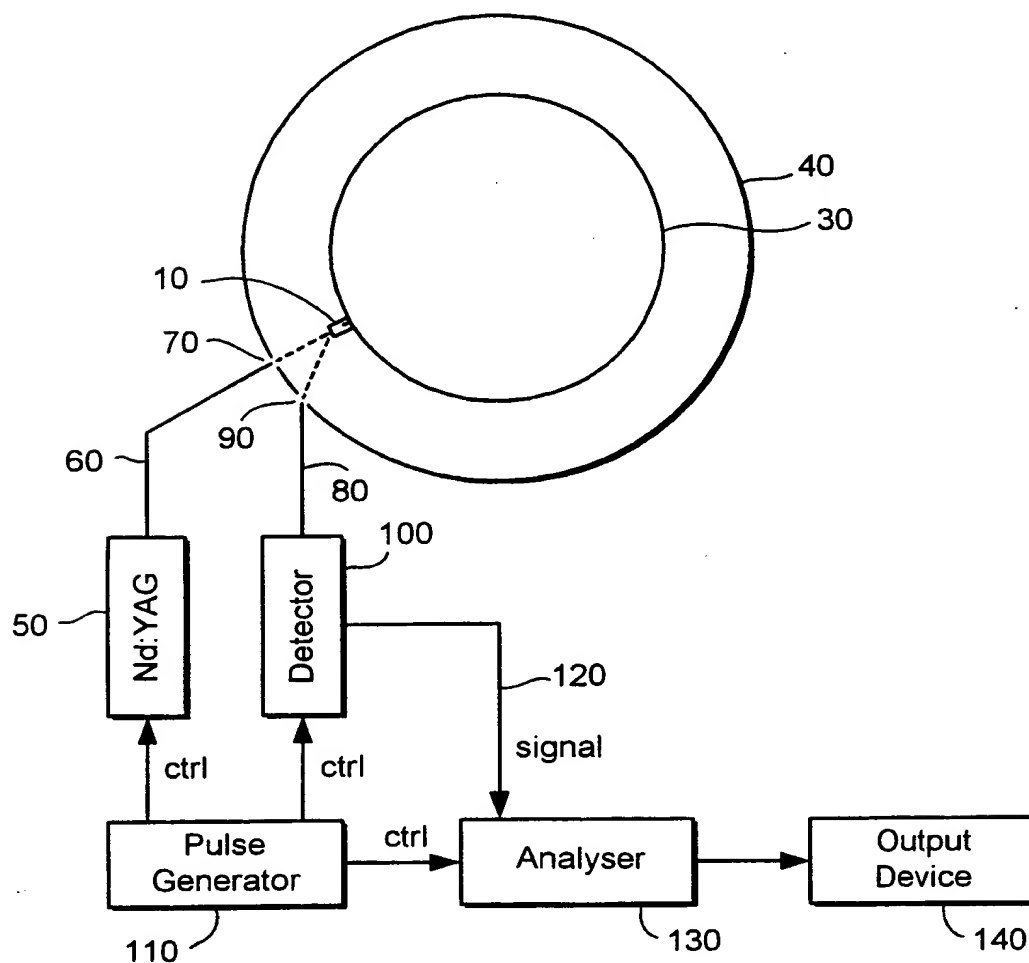


FIG. 2

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2 / 7

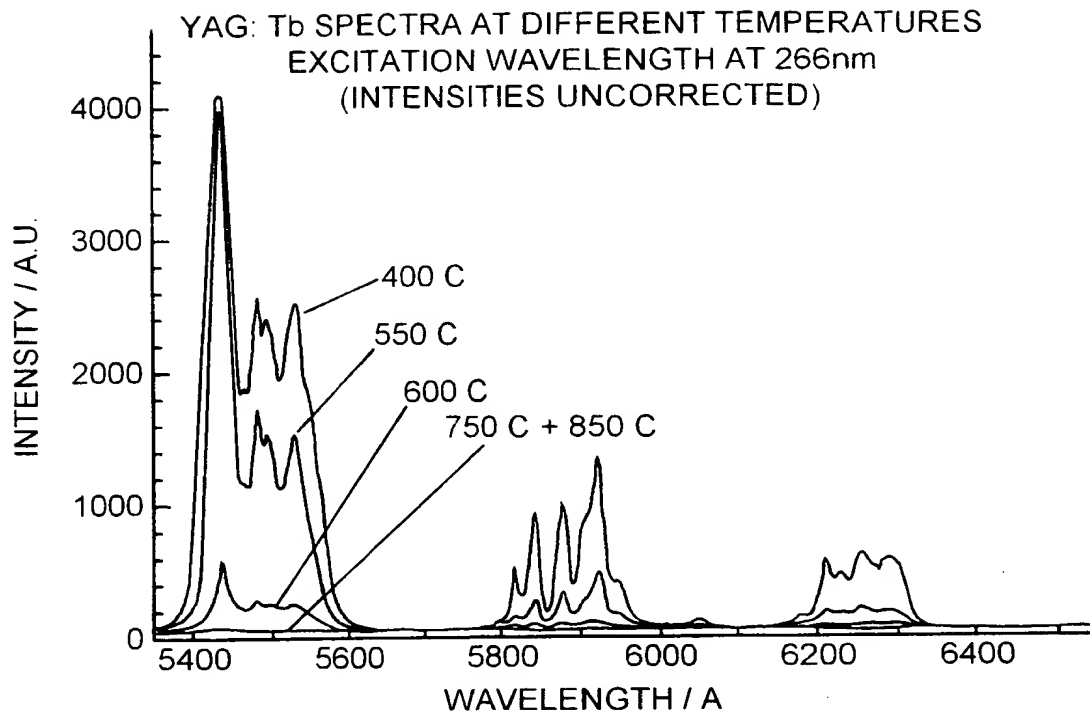


FIG. 3

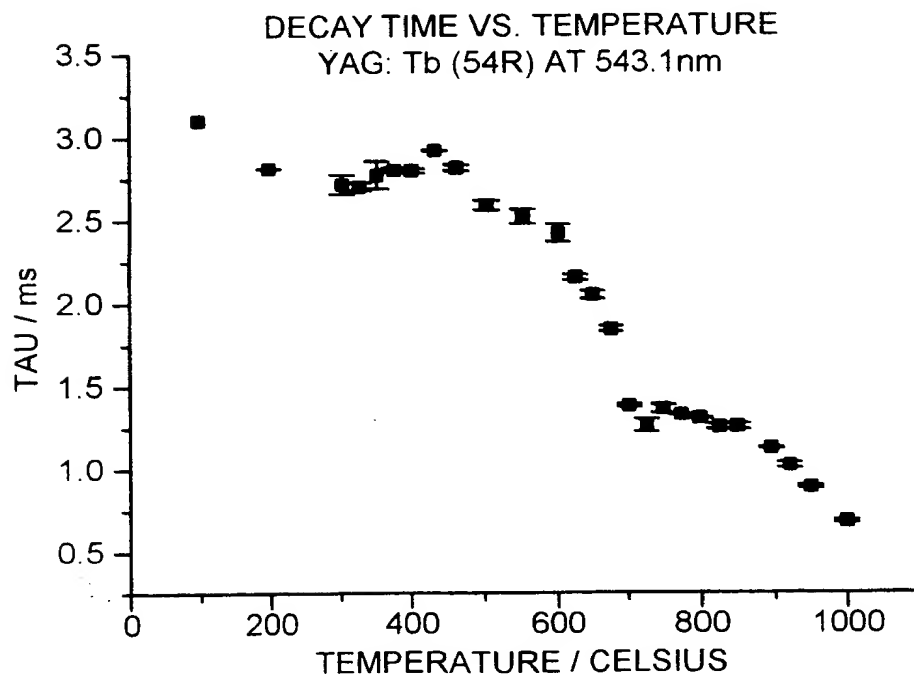


FIG. 4

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3 / 7

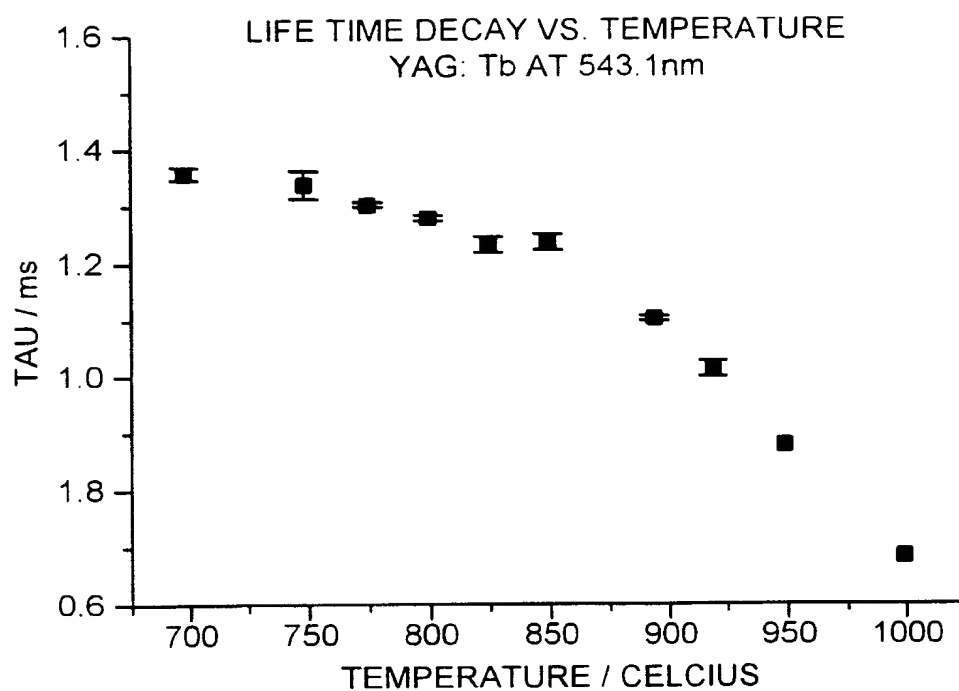
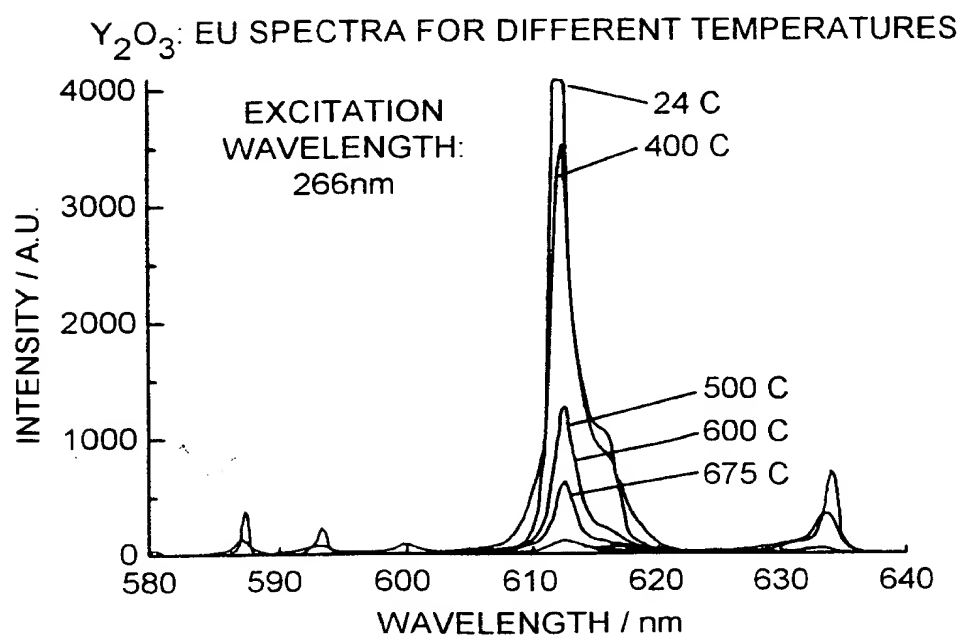


FIG. 5



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4 / 7

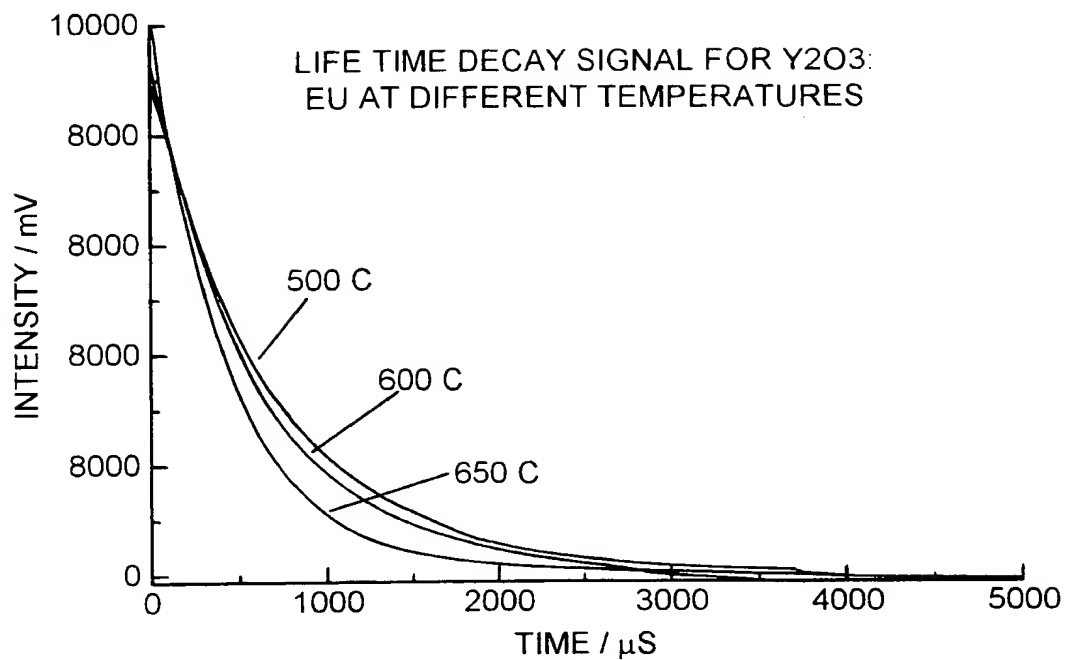


FIG. 7

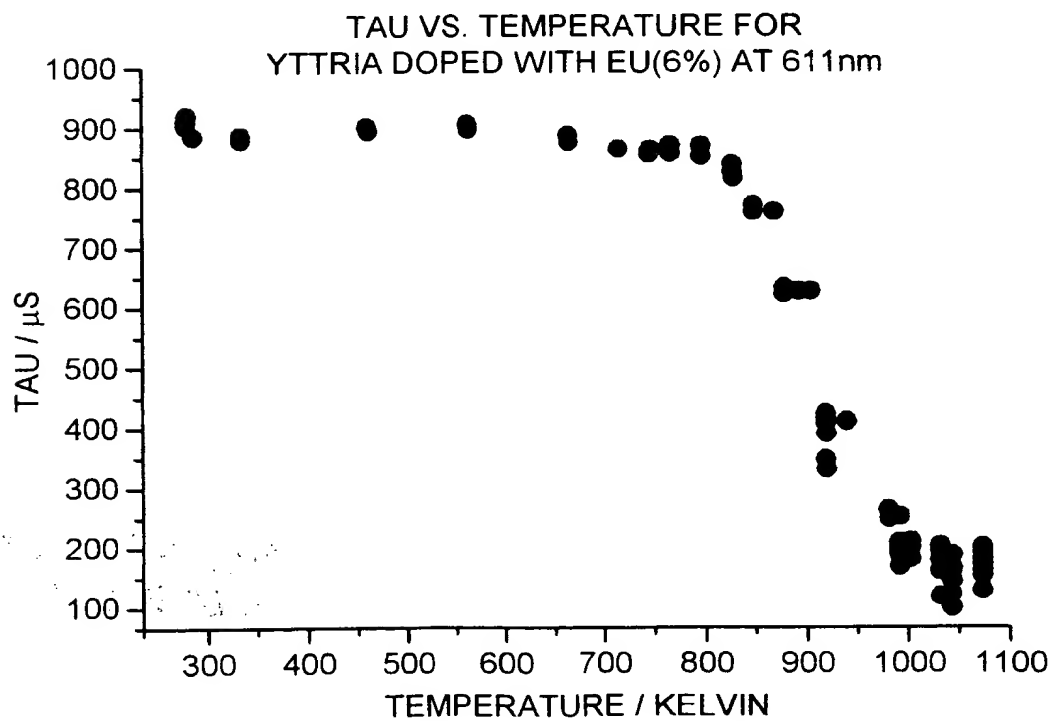


FIG. 8

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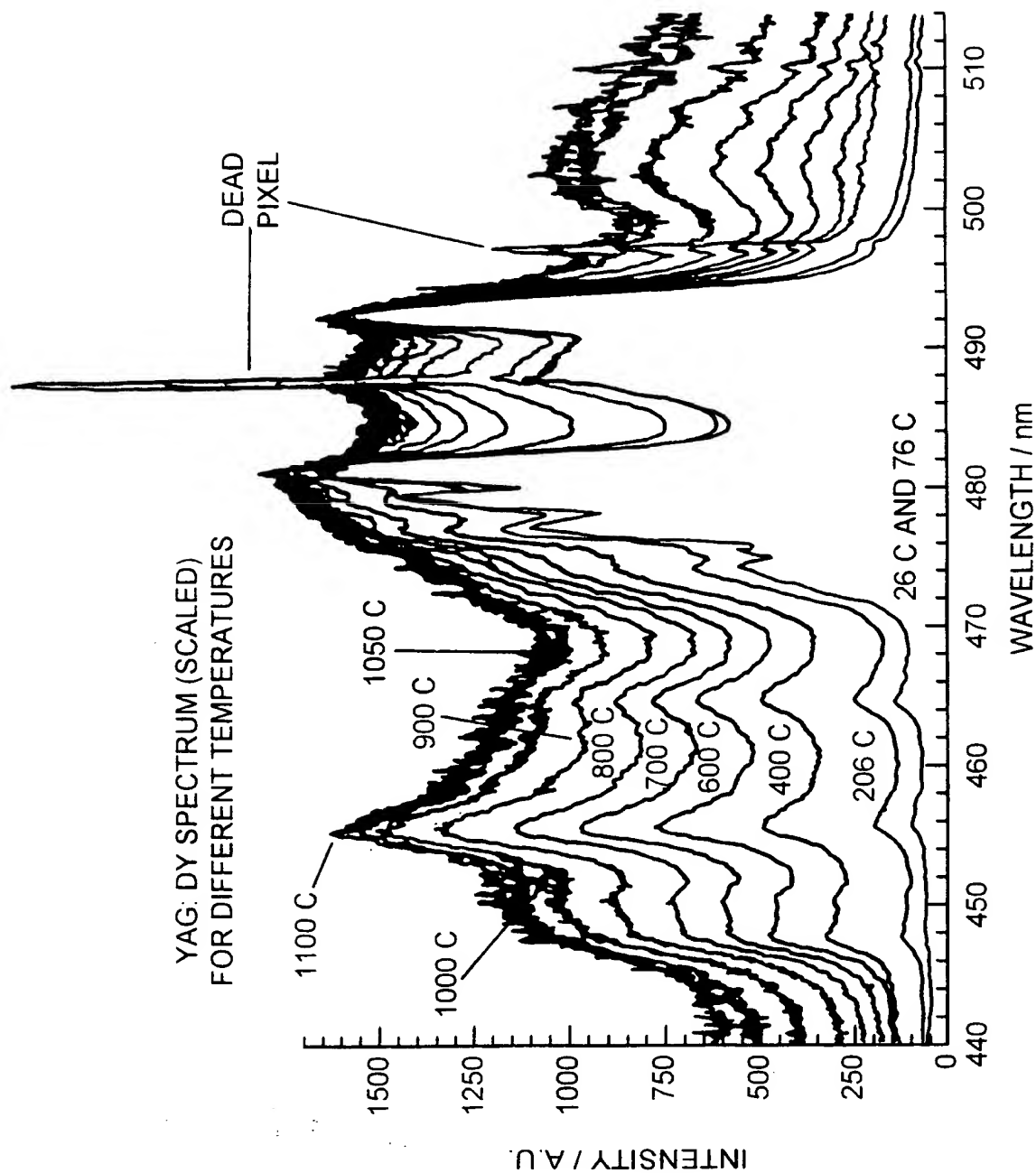


FIG. 9

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6 / 7

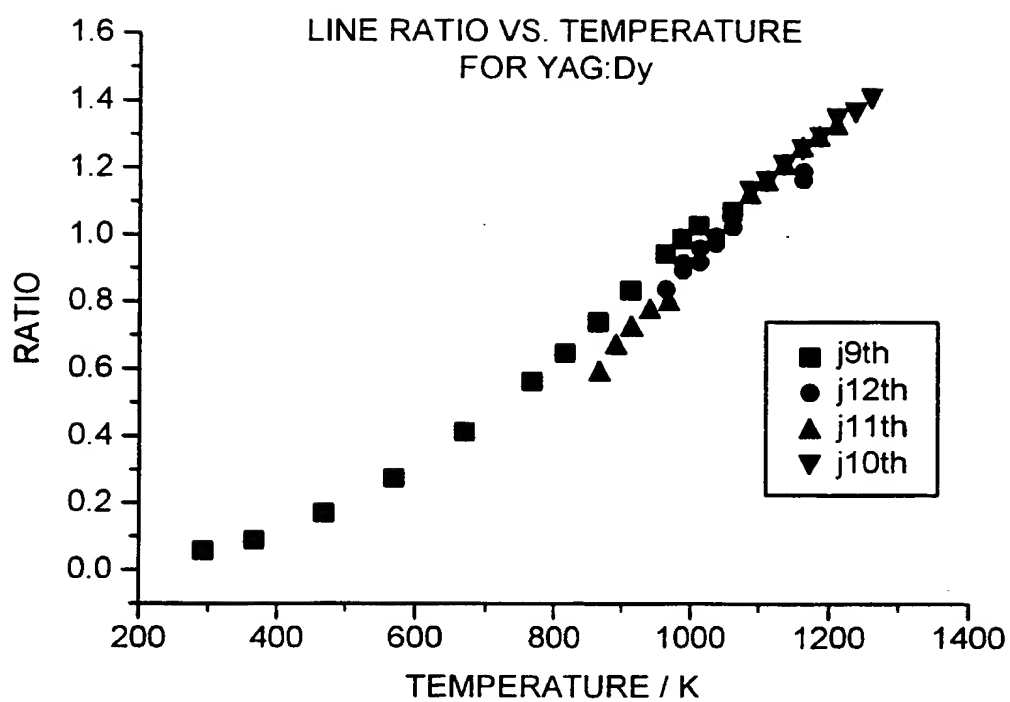


FIG. 10

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7 / 7

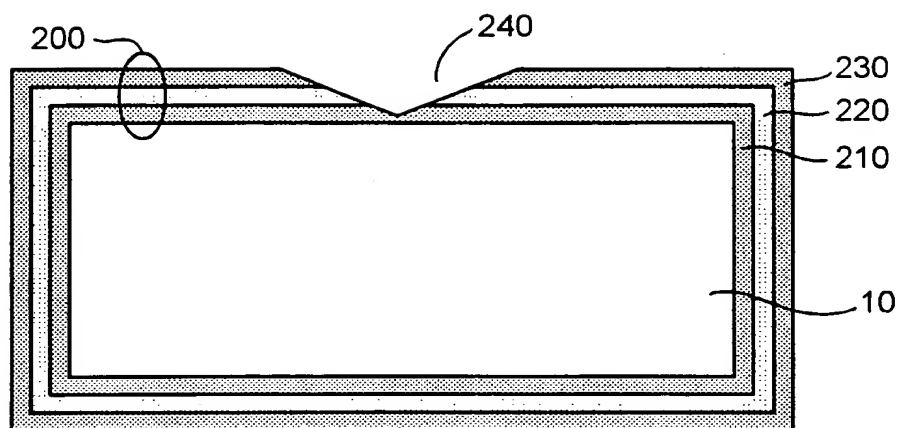


FIG.11

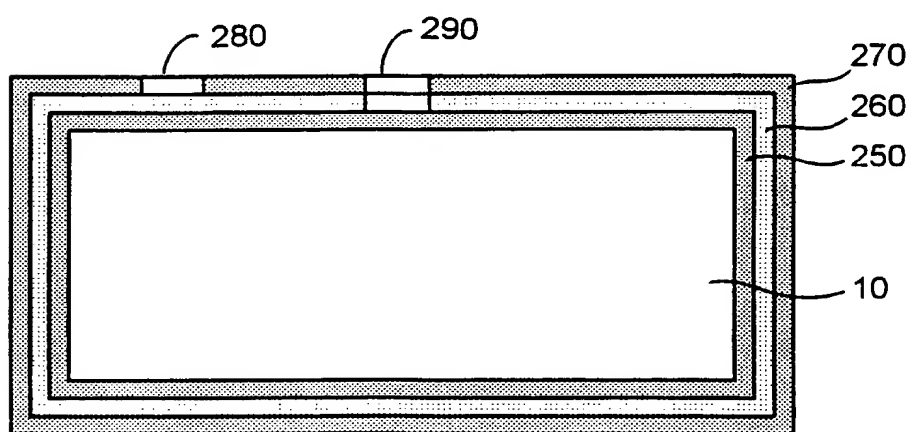


FIG.12

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02413

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C30/00 G01K11/20 G01K11/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C G01K C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 730 528 A (ALLISON STEPHEN W ET AL) 24 March 1998 (1998-03-24)	1,3-5, 7-10,14, 15,18-21 6,11,13 16,17
Y	abstract	
A	column 1, line 18 - line 21 column 1, line 42 - line 49 column 2, line 1 - line 39 column 3, line 30 - line 49 column 4, line 19 - line 49 column 5, line 7 -column 6, line 41 column 7, line 62 -column 8, line 13 column 8, line 47 - line 56 claims; figures --- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

27 September 1999

Date of mailing of the international search report

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Ceulemans, J

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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